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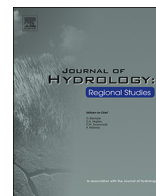
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Isotopic and geochemical surveys of lakes in coastal B.C.: Insights into regional water balance and water quality controls

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ABSTRACT

Study region: This study was conducted within a 100,000 km² area of British Columbia, (B.C.) Canada including Vancouver Island, the Georgia Basin, and the Pacific and Kitimat mountain ranges rising from the Pacific Ocean.

Study focus: A stable isotope mass balance method is applied to estimate evaporation loss and water yield from a remote network of 560 lakes on Vancouver Island and coastal B.C., based on helicopter sampling surveys conducted between 2008 and 2015. Spatial patterns in derived hydrological parameters are compared to water quality indicators and watershed characteristics to provide insight into water quantity and water quality relationships in the region, to be incorporated within a future critical loads assessment.

New hydrological insights for the region: Regional trends in lake water balance, underlying physical drivers, and geochemical processes potentially influencing critical loads of acidity are described. Dominant non-anthropogenic regional drivers of geochemistry include sea spray, lithology, weathering and elevation. Significant contrast is noted in alkalinity between the sedimentary and volcanic substrates on Vancouver Island and igneous intrusive substrates of the Pacific and Kitimat ranges. A positive correlation is found between elevation and water yield to lakes, while the opposite is observed for rivers, which is interpreted to reflect disconnection of low elevation lakes from regional drainage networks. This may invalidate use of river gauge data for critical loads assessment in this or similar regions.

1. Introduction

Lakes are an important element of the landscape in coastal B.C. accounting for close to 10% of the land area, although relatively few studies have described the hydrology and water quality of these lakes. While a limited number of local studies have been conducted to characterize specific lakes and water supply reservoirs on southern Vancouver Island (Nowlin et al., 2004; Werner et al., 2015), and selected lake types such as proglacial lakes (Richards et al., 2012), fjord-type lakes (Petticrew et al., 2015) or sub-alpine lakes (Dunnington et al., 2016), no studies have previously investigated regional patterns in lake water balance parameters across the region. In fact, most hydrological interest in B.C. has been focused on the Okanagan valley due to water scarcity in this region (see Wassenaar et al., 2011). While many areas of coastal B.C. are still considered pristine and undeveloped, dominance of base-poor geologies with poor weathering capacity and potential for rapid growth in emissions due to expansion of shipping, industry and

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urbanization in the south coastal mainland, indicate that soils and lakes in some areas may be at risk of acidification (Mongeon et al., 2010).

Here, we report on a systematic survey of lakes in coastal B.C. designed to provide a regional assessment of critical loads of acidity to lakes as part of Canada's National Acid Rain Program. Acid sensitivity studies within the program have mainly focused on eastern Canada over the past several decades, largely owing to proximity to emissions from intensive industrial activity in eastern Canada and the United States. Only a few studies have been carried out recently in western Canada (Jeffries et al., 2010). In a national assessment preceding initiation of this study, Jeffries et al. (2005) concluded that the information available for evaluating the regional acidification status of lakes in many parts of western Canada was too old, too sparse or too unrepresentative to permit meaningful analysis, and new and representative surveys were recommended. As a result, new surveys were initiated in Alberta, Saskatchewan and Manitoba see Gibson et al. (2010a,b), Jeffries et al. (2010)). An additional study was initiated in coastal B.C., an area potentially sensitive to local, marine and transboundary acidifying emissions (Environment Canada and U.S. Environmental Protection Agency, 2014).

The purpose of this paper is to provide an introduction to the B.C. survey results describing some of the major regional hydrologic patterns across the region and their relation to climatic and physical characteristics of the selected lakes and watersheds, and the lake water geochemistry. The hydrologic assessment applies an isotope mass balance approach relying on measurement of the stable isotopes of water, $\delta^{18}\text{O}$ and $\delta^2\text{H}$, in lakewater, which has been previously tested across other regions of Canada and the US. (Gibson et al., 2010a,b; Gibson et al., 2017; Brooks et al., 2014). The stable isotopes, which are contained within the water molecule, are used to estimate water yield to the lakes based on a steady-state isotope mass balance model (Gibson et al., 2015a), and provide a new perspective of hydrologic variability of a large number of lakes and contributing watersheds that have not previously been studied in detail. In addition, this study provides an initial evaluation of the main drivers of water chemistry of the lakes including physical characteristics of the watersheds and water balance parameters. This analysis will underpin an assessment of critical loads of acidity for lakes in the region using the Henriksen et al. (2002) model and isotope-based estimates of water yield.

1.1. Study area

The study area lies in coastal B.C. between 48°N and 58°N and 124°W and 138°W, including Vancouver Island and coastal regions of B.C. between the Alaska State border to the north and the Washington State border to the south. 560 lakes were sampled in total (Fig. 1), ranging in size from less than 0.1–124 km², situated at elevations ranging from 18 to 2003 m above sea level (m.a.s.l.) The watersheds of the study lakes ranged in size up to 1534 km², averaging 15 km².

The study area occurs predominantly on the windward (westward) slopes of the coastal mountains, and has a cool mesothermal climate with cool summers and mild winters (Pojar et al., 1991a). Mean annual temperature ranges from 0.5 to 14 °C, averaging 9.1 °C as interpolated from the gridded North American Regional Reanalysis (Mesinger et al., 2006). Precipitation has strong inland and northward gradients, ranging from 600 mm in areas of the Georgia Basin with significant rainshadow effects to 3400 mm in the

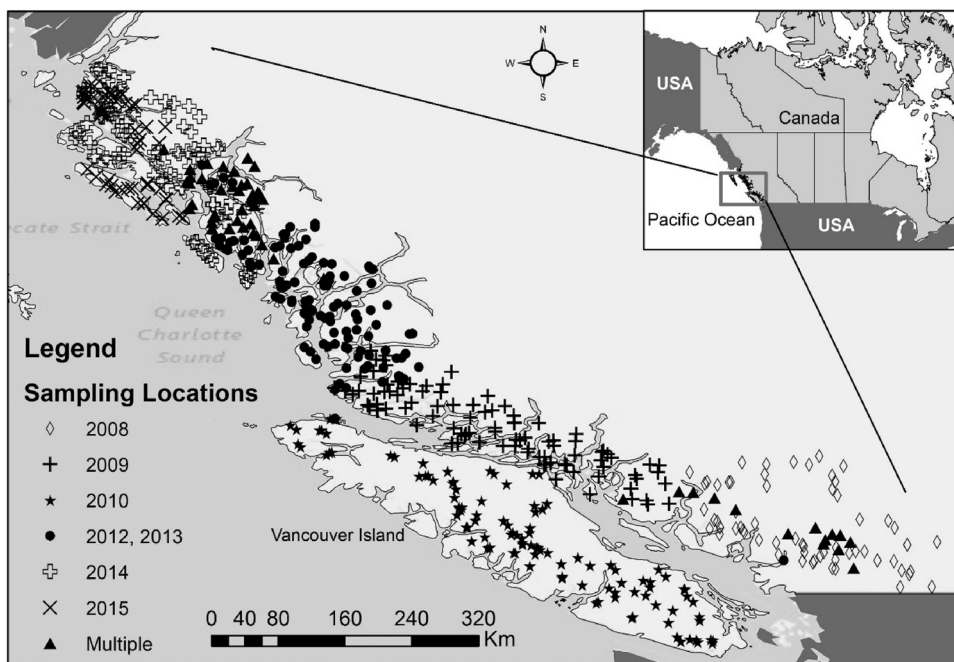


Fig. 1. Map of coastal B.C. showing lakes sampled in this study, as differentiated by year of first sampling. Lakes sampled multiple times are also identified.

northernmost areas in the vicinity of Prince Rupert, which is on average among the highest annual rainfall areas of B.C. Relative humidity is variable ranging from 66% to 88%, averaging 79% (Mesinger et al., 2006).

Within the national ecozone classification, the study area lies within the Pacific Maritime Ecozone which is dominated by coastal mountains, rising steeply from fjords and deep channels lining the coast, and with glaciers and snowfields capping the tallest ranges (Wiken, 1986). From the biogeoclimatic classification widely used within B.C., the area is mainly within the coastal Western Hemlock zone between sea level and 900 m, and predominantly within the Mountain Hemlock zone in sub-alpine areas (Pojar et al., 1987, 1991a, 1991b). Steep precipitation and continentality gradients are evident, with wetter maritime areas being dominated by Western hemlock, amabilis fir, western redcedar, and Sitka spruce, while drier maritime forests typically contain a substantial component of Douglas-fir (Pojar et al., 1991a).

Tree growth is progressively poorer with increasing elevation due to a shorter growing season, prolonged snow cover, and cooler temperatures (Pojar et al., 1991b). Soils within our study watersheds are 80% podzolic, most being Humo-Ferric Podzols which, with increasing precipitation, grade into Ferro-Humic Podzols (see Pojar et al., 1991a).

Bedrock along the coastal mountain ranges is dominated by intrusive igneous rocks, with occurrence of metamorphic, sedimentary and volcanic rocks. Ultramafic rocks are generally absent in the majority of watersheds sampled. Vancouver Island watersheds are distinct in that bedrock is predominantly comprised of volcanic and sedimentary rocks (B.C., Ministry of Forests, Lands and Natural Resource Operations, 2017).

Lakes are important features of the landscape in coastal B.C., occupying roughly 10% of the land surface in the study region. A total of 18 land cover classifications are distinguished in these watersheds, including alpine, subalpine, old forest, young forest, freshwater and recently logged lands.

1.2. Surveys and lake selection

Helicopter surveys to collect lake water were conducted in September–October each year between 2008 and 2015, with the exception of 2011. Lake selection focused on areas with poorly weatherable bedrock geology where the waterbodies are expected to be particularly sensitive to or already influenced by atmospheric deposition. Within the study area, lake locations, surface areas and geographic identifiers were extracted from the B.C. Ministry of Environment Watershed Atlas (B.C., Ministry of Forests, Lands and Natural Resource Operations, 2017). Lake buffering capacity was estimated by overlaying the lake layer and a derived weathering class layer. Using 1:250 000 digital bedrock geology layers available from the B.C. Ministry of Mines and Petroleum Resources (2005), regional bedrock was divided into five weathering classes (WC) based on Nanus and Clow (2004): a) WC1–low to no buffering capacity (e.g., granite, schist), b) WC2–moderate buffering capacity (e.g., diorite, gneiss), c) WC3–high buffering capacity (e.g., gabbro, basalt), d) WC4–very high buffering capacity (e.g., amphibolites, hornblende) and, e) WC5–extremely high buffering capacity (e.g., marble, limestones). Lakes with more sensitive underlying geologies, i.e. WC1, WC2, WC3, were targeted in the lake selections.

A stratified-random sampling methodology was used to select lakes within this target population. Lakes were selected from five defined size classes (4–10 ha; 10–50 ha; 50–100 ha; 100–500 ha; > 500 ha) applying a four-part selection criteria described previously (Jeffries et al., 2010). Overall, the number of lakes sampled represented approximately 10% of the population of lakes greater than 4 ha surface area in the study area.

2. Methods

2.1. Water sampling and analysis

Water samples were 2-L grab samples in pre-cleaned plastic bottles taken approximately centre-lake from a float-equipped Bell 206 helicopter using a dipper plunged to 1-m depth (2008–2012) or filled using a small pump submerged to 1-m depth (2013–2015). Positions were obtained using a Garmin 76S™ global positioning unit (GPS), lake surface elevation was recorded from the aircraft altimeter, and water depth at the sample site was measured using an Eagle Cuda™ depth sounder with transducer mounted to the helicopter float. Surface temperature, conductivity and pH were measured *in situ* using a Yellow Springs Instrument Model probe, calibrated in the morning before each field day. At the conclusion of the flight, subsamples were transferred to 30-mL high-density polyethylene (HDPE) bottles for isotopic analysis, with the majority of the sample then being selectively filtered and transferred to HDPE bottles for various geochemical analysis by standard methods (CCME, 2011). Inorganic analyses were filtered to 0.45 µm using cellulose-acetate filters, whereas total nutrients were not filtered. Samples were kept cool and shipped to laboratories as soon as possible, normally within one day.

In 2008, major ions and nutrients were analyzed at ALS Analytical Laboratories in Vancouver, B.C. From 2009 to 2015, analyses were conducted at the Pacific Environmental Science Centre (PESC), an Environment Canada laboratory in North Vancouver, B.C. Hold time prior to analyses was typically several days. Stable isotopes ($^{16}\text{O}/^{18}\text{O}$ and $^2\text{H}/^1\text{H}$) were analyzed either at the Environmental Isotope Laboratory, University of Waterloo, Waterloo, ON (2008) or at InnoTech Alberta, Victoria, B.C. (2009–2015). All water samples were analyzed by Isotope Ratio Mass Spectrometry, the vast majority using a Thermo Scientific Delta V Advantage Dual Inlet/HDDevice isotope ratio mass spectrometer. In all cases, isotopic analyses were made within three months of sample collection. Results are reported in δ notation in permil (‰) relative to Vienna Standard Mean Ocean Water (V-SMOW) and normalized to the SMOW-SLAP scale where SLAP is Standard Light Arctic Precipitation (see Coplen 1996). Analytical uncertainty is estimated to be better than $\pm 0.1\text{‰}$ for $\delta^{18}\text{O}$ and $\pm 1\text{‰}$ for $\delta^2\text{H}$.

Dissolved major cations and anions were determined by ion chromatography. Total nitrate (TN) and total phosphorus (TP) were

measured by flow-injection analysis. In 2008, dissolved organic carbon (DOC) was quantified by combustion of 0.45 μm cellulose-acetate membranes, while in 2009–2015, DOC was calculated as the difference between dissolved carbon (DC) and dissolved inorganic carbon (DIC) measured by combustion. Alkalinity was determined by Gran Titration. Quality assurance and quality control (QA/QC) measures included blank and field duplicate sample submissions. A total of 223 water samples were collected as duplicates and for QA/QC purposes, specifically to establish the uncertainty associated with using a one-time sampling strategy. Incoming analytical data were assessed using concordance of duplicate results and, for dissolved ions, charge balances.

2.2. Isotope mass balance

Hydrology of each lake was characterized using an isotope mass balance (IMB) model developed under the assumption of a well-mixed water body and steady-state conditions, which has been demonstrated previously for shallow lakes in northern Canada (Gibson et al., 2002, 2010a,b, 2015a, 2017; Bennett et al., 2008). The IMB is used to estimate evaporation/inflow based on the isotopic offset between lake water and precipitation input. Then precipitation, evaporation, and relative humidity estimates are extracted for each site based on a gridded climate dataset, and lake and watershed area estimates are incorporated to constrain the ungauged inflow to the lake and resulting outflows.

The annual water and isotope balances for a well-mixed lake in isotopic and hydrologic steady state can be written, respectively as:

$$I = Q + E \text{ (m}^3\text{.yr}^{-1}\text{)} \quad (1)$$

$$I\delta_I = Q\delta_Q + E\delta_E \text{ (%o.m}^3\text{.yr}^{-1}\text{)} \quad (2)$$

where I , Q and E are lake inflow, discharge and evaporation rates ($\text{m}^3\text{.yr}^{-1}$), and δ_I , δ_Q and δ_E are the isotopic compositions of inflow, discharge and evaporation fluxes (%o), respectively. Note that $I = P + R$ where P is precipitation on the lake surface and R is ungauged inflow to the lake. We can rearrange Eq. (2), and substitute $Q = I - E$ from Eq. (1) to yield:

$$E/I = (\delta_I - \delta_Q)/(\delta_E - \delta_Q) \text{ (dimensionless)} \quad (3)$$

where E/I is the evaporation to inflow ratio. For well-mixed lakes we have often assumed $\delta_Q \approx \delta_L$ where δ_L is isotopic composition of the lake. For headwater lakes, the isotope composition of inflow is approximated by that of precipitation, i.e. $\delta_I \approx \delta_P$, whereas the isotopic composition of lake evaporate δ_E is estimated using the Craig and Gordon (1965) model given by:

$$\delta_E = ((\delta_L - \varepsilon^+)/\alpha^+ - h\delta_A - \varepsilon_K)/(1 - h + 10^{-3}\cdot\varepsilon_K) \text{ (%o)} \quad (4)$$

where h is relative humidity (decimal fraction), δ_A is isotopic composition of atmospheric moisture (%o), ε^+ is equilibrium isotopic separation (%o; see Horita and Wesolowski, 1994), α^+ is the equilibrium isotopic fractionation, where $\varepsilon^+ = \alpha^+ - 1$, and ε_K is the kinetic isotopic separation (%o; see Horita et al., 2008). Substitution of δ_E into Eq. (3) yields:

$$x = E/I = (\delta_L - \delta_I)/(m(\delta^* - \delta_L)) \text{ (dimensionless)} \quad (5)$$

where

$$m = (h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^+/\alpha^+))/(1 - h + 10^{-3}\cdot\varepsilon_K) \text{ (dimensionless)} \quad (6)$$

and

$$\delta^* = (h\delta_A + \varepsilon_K + \varepsilon^+/\alpha^+)/(h - 10^{-3}\cdot(\varepsilon_K + \varepsilon^+/\alpha^+)) \text{ (%o)} \quad (7)$$

As the inflow to a lake is comprised of precipitation on the lake surface, P , as well as ungauged inflow, R , i.e. $I = P + R$, we can estimate R for headwater lakes by substitution of Eq. (5):

$$R = E/x - P \text{ (m}^3\text{.yr}^{-1}\text{)} \quad (8)$$

where $E = eLA$ and $P = pLA$; e and p are the annual depth-equivalent of evaporation and precipitation (m.yr^{-1}), and LA is the lake area (m^2). Water yield, or the depth-equivalent runoff, can then be estimated as

$$WY = R/WA \cdot 1000 \text{ (mm.yr}^{-1}\text{)} \quad (9)$$

where WA is the watershed area. For non-headwater lakes, owing to the fact that many receive a portion of isotopically enriched water from upstream lakes, the water yield estimates should be regarded as a lower limit. Lakes sampled in this survey were not likely influenced significantly by this factor as they were predominantly headwater lakes.

Isotopic composition of atmospheric moisture δ_A is estimated by fitting predicted enrichment to the observed local evaporation line based on a partial equilibrium approach (see Gibson et al., 2015a). This approach accounts for seasonality observed in evaporation losses to the atmosphere.

2.3. Climate and watershed parameters

Climate parameters were obtained from the 32-km resolution North American Regional Reanalysis (NARR) dataset (Mesinger

et al., 2006). Monthly climatology (based on data from 1979 to 2003) was extracted for the grid cells corresponding to the location of each of the study lakes. The parameters extracted were (i) surface total precipitation (mm yr^{-1}), (ii) 2-m relative humidity (%), (iii) surface evaporation (mm yr^{-1}), and (iv) 2-m temperature (K). The evaporation flux-weighting approach (see Gibson et al., 2015b) was used to weight estimates of relative humidity and temperature so that the water balance calculations were representative of the open water season. Temperature and precipitation values interpolated from the NARR dataset, which has been used in numerous isotope-based assessments across Canada (Gibson et al., 2010a,b, 2015b, 2016, 2017; Jeffries et al., 2010; Scott et al., 2010) were also compared to that derived from the gridded 800-m resolution PRISM climatology (Pacific Climate Impacts Consortium et al., 2014), as this dataset has been widely applied by some research groups working in B.C. Overall, we found that isotope-based estimates of water yield differed by less than 5% on average between the two climate datasets, but was most pronounced below 200 mm yr^{-1} . Based on this similarity we suggest that either dataset may be used effectively for the purposes of a regional assessment.

Application of the IMB model also requires delineation of the watershed areas, lake areas, and lake elevations for each of the study lakes. Using the coordinates (latitude – longitude) for each lake, watershed area, lake area, and lake elevation were obtained using digital elevation data in raster format from 1:50,000 Canada National Topographic Series (NTS) map sheets. Canadian National Hydro Network data in vector format were obtained from the GeoBase portal (Canada, Natural Resources Canada, 2017). Terrain preprocessing to incorporate the vector hydrographic network and to fill small sinks was required before the Digital Elevation Model (DEM) could be used for efficient watershed delineation (see Jeffries et al., 2010).

Individual watersheds were delineated in the ArcGIS program using the ArcHydro tools, where each watershed was delineated upstream of a lake outlet. Hydrographic and elevation datasets were used to depict the lake outlet locations. In some cases two or more partial watersheds had to be merged together to create a final watershed polygon. The planimetric area of both the lake and watershed polygons was calculated in the ArcGIS program based on the equal area projection.

2.4. Isotopic parameters

Monthly precipitation $\delta^{18}\text{O}$ estimates were obtained for each lake location based on empirically derived global relationships between latitude and elevation (Bowen and Wilkinson, 2002) fitted to regional precipitation data from the Canadian Network for Isotopes in Precipitation (see Birks and Gibson, 2009). The $\delta^2\text{H}$ composition of monthly precipitation was calculated assuming that precipitation would follow the relationship defined by the Global Meteoric Water Line (GMWL; Craig, 1961). Annual averages of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in precipitation were amount-weighted using monthly precipitation obtained from the NARR dataset. Note that calculations were performed using the long-term climatology of all parameters.

2.5. Correlation and PCA analysis

We analyzed the relationships between physical and geochemical properties, land cover, isotopic characteristics and derived water properties to investigate and better understand controlling processes in the lakes and their watersheds. A Spearman rank order test was used to test correlations as several of the variables were non-linearly related or were not normally distributed.

Principal Component Analysis (PCA) was also applied, a technique described in detail by Mardia et al. (1989). For this study, as noted below, variables included in the PCA included: (i) climate properties; (ii) physical characteristics and land cover; (iii) geochemical properties; and (iv) isotopes and derived hydrologic properties. Some geological characteristics such as bedrock coverage were not included in the PCA due to lack of consistent information in all areas. Several variables that were highly correlated with others, such as $\delta^2\text{H}$ with $\delta^{18}\text{O}$, were not included. As a result, 24 variables were used, including, by class: (i) evaporation-flux-weighted temperature (T.FW, °C), evaporation-flux-weighted relative humidity (RH.FW, %), precipitation (P.m, m/year), evaporation (E.m, m/year); (ii) elevation (Ele, m.a.s.l.), watershed area (WA, km^2), Lake area/watershed area (LAWAR, dimensionless), subalpine area (Sub.Alpine, %), freshwater area (F.water, %), old forest area (Old.Forest, %), young forest area (Y.Forest, %), and recently logged area (Logged.R, %); (iii) electrical conductivity (EC, $\mu\text{S}/\text{cm}$), alkalinity (Alk, mg/L), chloride (Cl, mg/L), calcium (Ca, mg/L), potassium (K, mg/L), dissolved organic carbon (DOC, mg/L), total nitrogen (TN, mg/L), total phosphorus (TP, mg/L), percentage sea spray (PSS, %); and (iv) lakewater $\delta^{18}\text{O}$ (d18OL, ‰V-SMOW), evaporation/inflow (EI.18O, %), and water yield (WY, mm/year). Note that land cover classes were based on percentages in each watershed and PSS was based on the method of Wadleigh et al. (1994). Due to the large range of measurements and variable distributions of selected parameters, the compiled database is log transformed and scaled to unit variance prior to the PCA analysis. The transformation and standardization of raw data is necessary to achieve close-to-normal distributions, and to downweight effects of extreme values in the PCA analysis. The multi-variate analysis leads to multiple principal components that help to understand the variations and relationship of variables. The first principal component (Dim1), a linear combination of the original variables, explains the largest amount of variance in the dataset and the second principal component (Dim2) describes the second largest variation remaining in the dataset. When presenting PCA results, the projection of an individual sample onto the axes defined by principal components (Dim) is termed “score”, whereas the coefficient for each variable in the linear combination is called “loading” of the variable. In the score plot, lakes with similar characteristics tend to plot close to each other, while lakes with distinct characteristics are expected to be farther apart. Meanwhile, the loading plot is commonly used to examine the relation between variables, as highly correlated variables tend to point in the same direction in a loading plot.

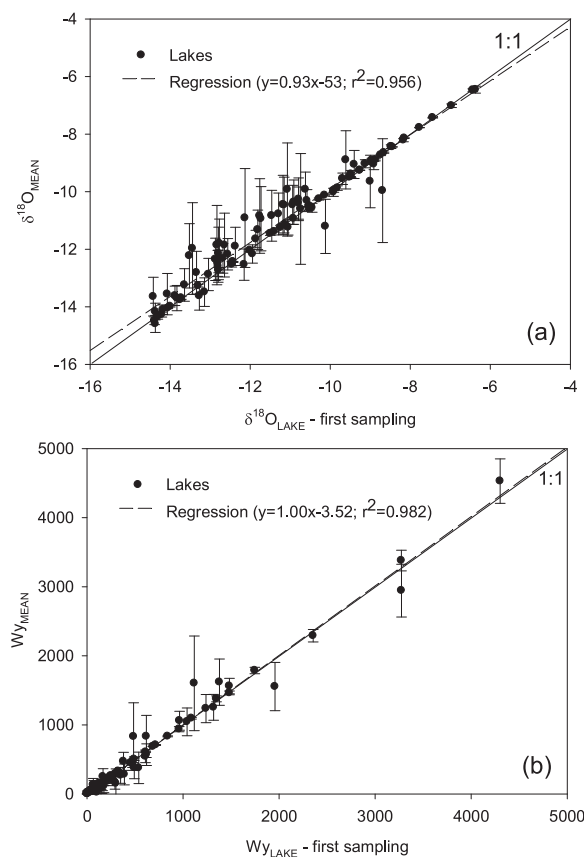


Fig. 2. Cross-plots showing temporal variability in (a) $\delta^{18}\text{O}$ of lakes; and (b) derived water yield to lakes. Repeat sampling was conducted in a subset of 100 lakes. Error bars depict ± 1 standard deviation of values measured on repeat samples.

3. Results and discussion

3.1. Repeat sampling

Prior to use in the regional assessment, it was important to evaluate whether one-time sampling was appropriate to characterize the water balance of most lakes, and if so, to determine the uncertainty associated with this approach. To evaluate this, a subset of data was assembled based on 100 lakes sampled on more than one occasion during the course of the study (2008–2015). 78 of the lakes were sampled twice, 10 lakes were sampled 3 times, and the remainder were sampled between 4 and 9 times. Climatic, isotopic and geochemical data, and watershed parameters for these lakes were compiled and used to estimate water yield by Eq. (9). As shown for $\delta^{18}\text{O}$ and for water yield (Fig. 2), a high degree of autocorrelation was found between the $\delta^{18}\text{O}$

values obtained from first-time and repeat sampling events ($\delta^{18}\text{O}$: $r^2 = 0.956$), which was also true for WY ($r^2 = 0.982$). Results in both cases were found to fall close to the 1:1 line suggesting that there was no systematic bias associated with this approach. Standard error for estimating $\delta^{18}\text{O}$ based on one-time sampling strategy is found to be $\pm 0.23\text{‰}$ (median value), which is close to the analytical uncertainty reported by many labs and only about 2% of the observed range of 12.6‰ for all lakes, while standard error in WY is estimated at ± 30 mm/year (median value). Mean standard error values are higher (± 0.44 for $\delta^{18}\text{O}$ and ± 115 mm/year for WY), but for WY are significantly impacted by extreme values owing to positively skewed distributions. In our judgement, repeat sampling results confirm that a one-time sampling approach is adequate for evaluating regional trends and can be applied with satisfactory confidence to differentiate lake-to-lake variations across the region and to meaningfully characterize water balance and evaporation patterns. While uncertainty associated with use of the annual steady-state method for estimating water balance of individual lakes has been shown to be in the range of ± 20 –30% (see Gibson et al., 2002; Jasechko et al., 2014), the resulting regional water yield distributions have been shown to be relatively robust, and we suggest are useful for capturing the expected range of regional runoff variability for evaluating critical loads (Gibson et al., 2010a,b, 2017).

3.2. Climate and watershed characteristics

Location (latitude and longitude) of the study lakes is shown to be fairly evenly distributed within the boundaries of the study area (Fig. 3a, b). Elevation distribution of the study lakes (Fig. 3c) is clearly shown to be positively skewed, attributed to lakes more

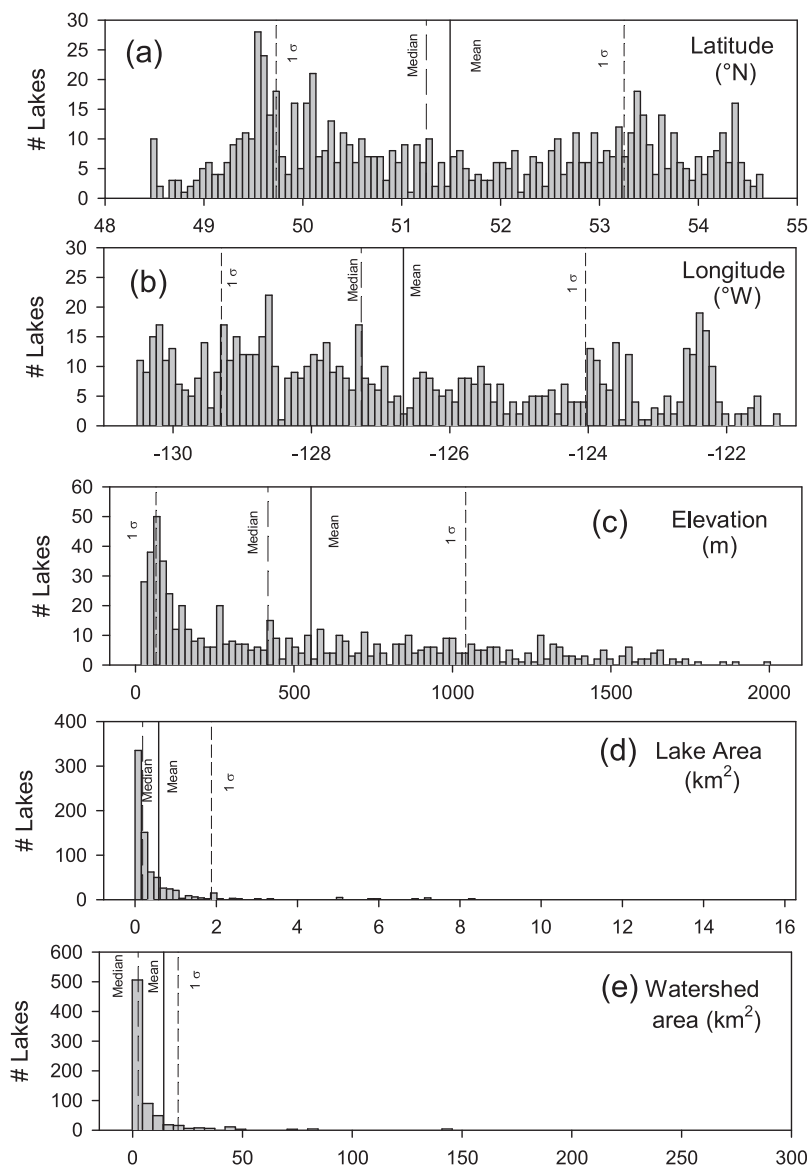


Fig. 3. Histograms showing distribution of lake and watershed characteristics, coastal B.C. Note that mean, median, and 1 standard deviations from mean are also indicated.

frequently being situated in valleys and low-lying areas in the landscape. Distribution of lake area and watershed area is similarly skewed (Fig. 3d, e), with average lake and watershed areas of 0.9 km^2 and 15 km^2 , respectively. However, the majority of lakes were less than 0.5 km^2 and watersheds less than 10 km^2 in area. Bemrose et al. (2009) reported positive skewness in watershed areas for Canada's river gauging network, although average gauged area for B.C. stations (including both active and discontinued), is significantly larger than the dataset reported here (3113 km^2). Large watersheds in this study, which ranged up to 1534 km^2 were found to be more commonly situated at lower elevations, and a slight increase in both lake size and lake/watershed area is noted towards higher elevations.

Histograms illustrating distribution of annual precipitation, lake evaporation and surface temperature reveal a wide range of variation across the study region (Fig. 4a, b, c, respectively), with precipitation being distinctly bimodal, but evaporation and temperature being unimodal and less systematic. Note that temperature shown is evaporation-flux-weighted according to the method of Gibson et al. (2008) and is therefore representative of conditions when lake evaporation was occurring. From both the precipitation and relative humidity datasets (Fig. 4a & d,) a distinct, low precipitation, low humidity region is evident, which corresponds to areas of the Georgia Basin, located inland from the mainland coast, which are characterized by a pronounced rain shadow effect associated with the Olympic and Cascade mountain ranges. Flux-weighted annual temperature for the sites ranges from less than 3°C for some alpine watersheds to 14°C for hyper-maritime watersheds. This is a slightly narrower range than mean annual temperature as it reflects average conditions when evaporation was occurring.

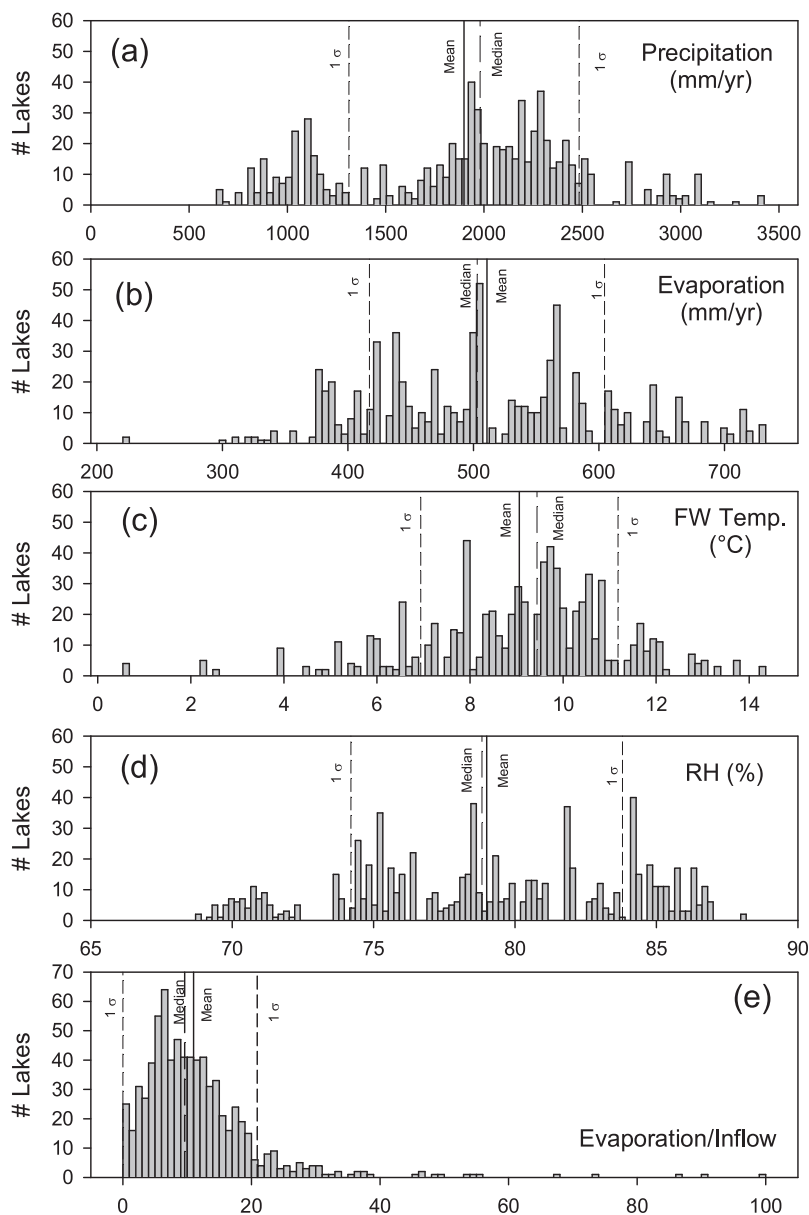


Fig. 4. Histograms showing distribution of climatic parameters, including annual precipitation, evaporation, evaporation-flux-weighted temperature and relative humidity, and the evaporation/inflow derived from isotope mass balance analysis.

3.3. Regional isotopic variations

Distributions of oxygen-18 and deuterium isotopic composition in precipitation (Fig. 5c, d), lake water (Fig. 5a, b), and atmospheric moisture (Fig. 5d, e) reveal a wide range in input signatures, evaporative enrichment of lake water, and atmospheric moisture conditions, respectively, for the study lakes. While isotopic composition of lakes is measured, we emphasize that isotopic composition of precipitation is modelled, *i.e.* based on amount-weighted $\delta^{18}\text{O}$ values interpolated from the CNIP network and constrained to fall on the GMWL (Craig, 1961). Atmospheric moisture is also modelled using the evaporation-flux-weighted approach of Gibson et al. (2008) to reflect conditions when lake evaporation was occurring.

Isotopic characteristics are also illustrated in ^2H – ^{18}O plots (Fig. 6). Relative to precipitation, which in our analysis is assumed to be well-represented by the GMWL, atmospheric moisture is depleted but also falls close to the GMWL, while only slight offset from the GMWL is measured in lakes. Lakes plot along local evaporation lines (LELs) with slopes ranging between 6.52 and 7.28 for individual sampling years (Table 1), varying spatially mainly according to atmospheric conditions in each specific sampling area.

Overall, the average slope of LELs is 6.98, and is steeper than observed in previous surveys of lakes in continental regions of Canada (Gibson et al., 2010a,b, 2015b, 2017) and the contiguous USA (Brooks et al., 2014), due mainly to consistently higher relative

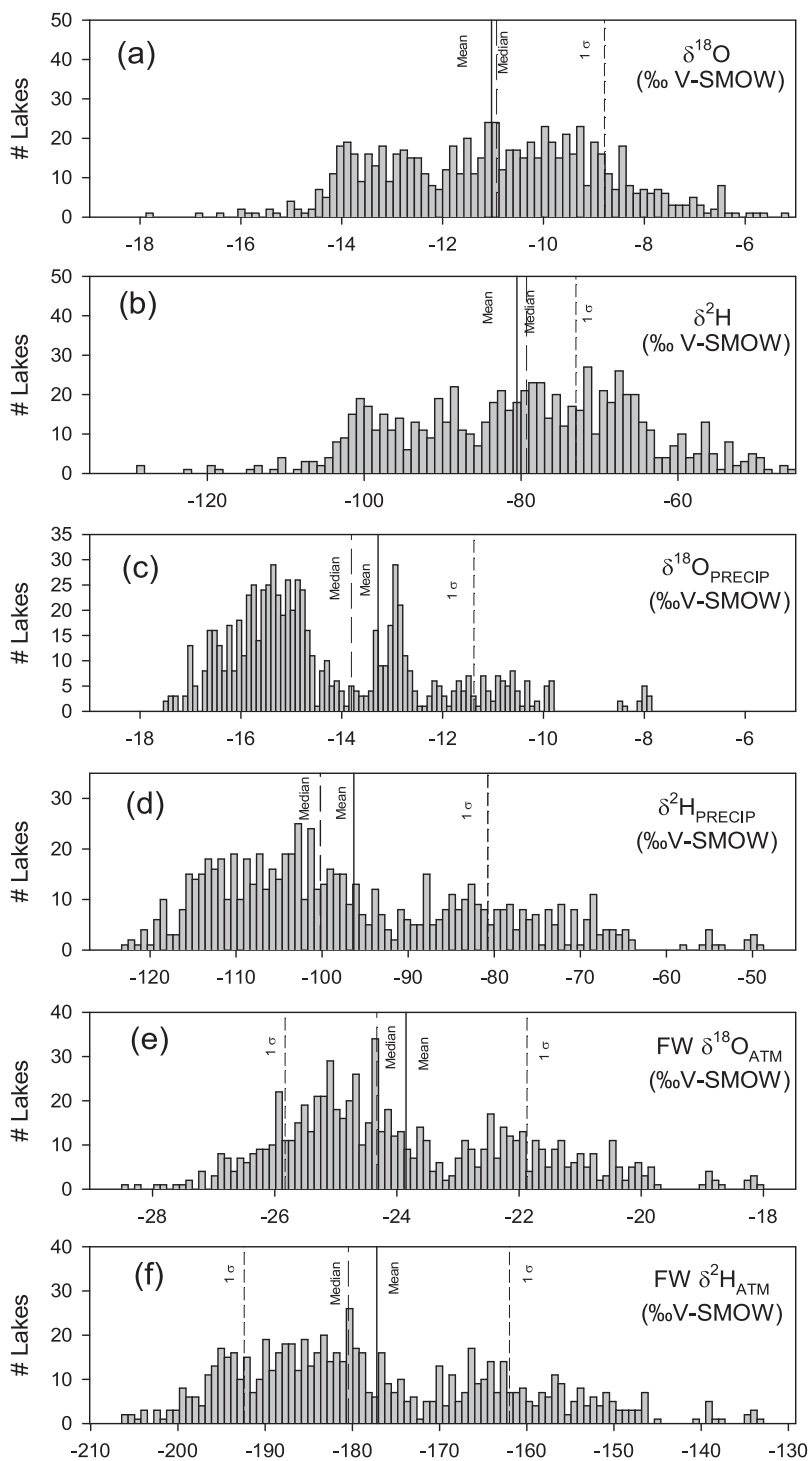


Fig. 5. Histograms showing distribution of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ measured in lake water, $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in modelled precipitation for each lake watershed, and $\delta^{18}\text{O}$ and $\delta^2\text{H}$ in evaporation-flux-weighted atmospheric moisture based on a partial equilibrium model. See text for discussion.

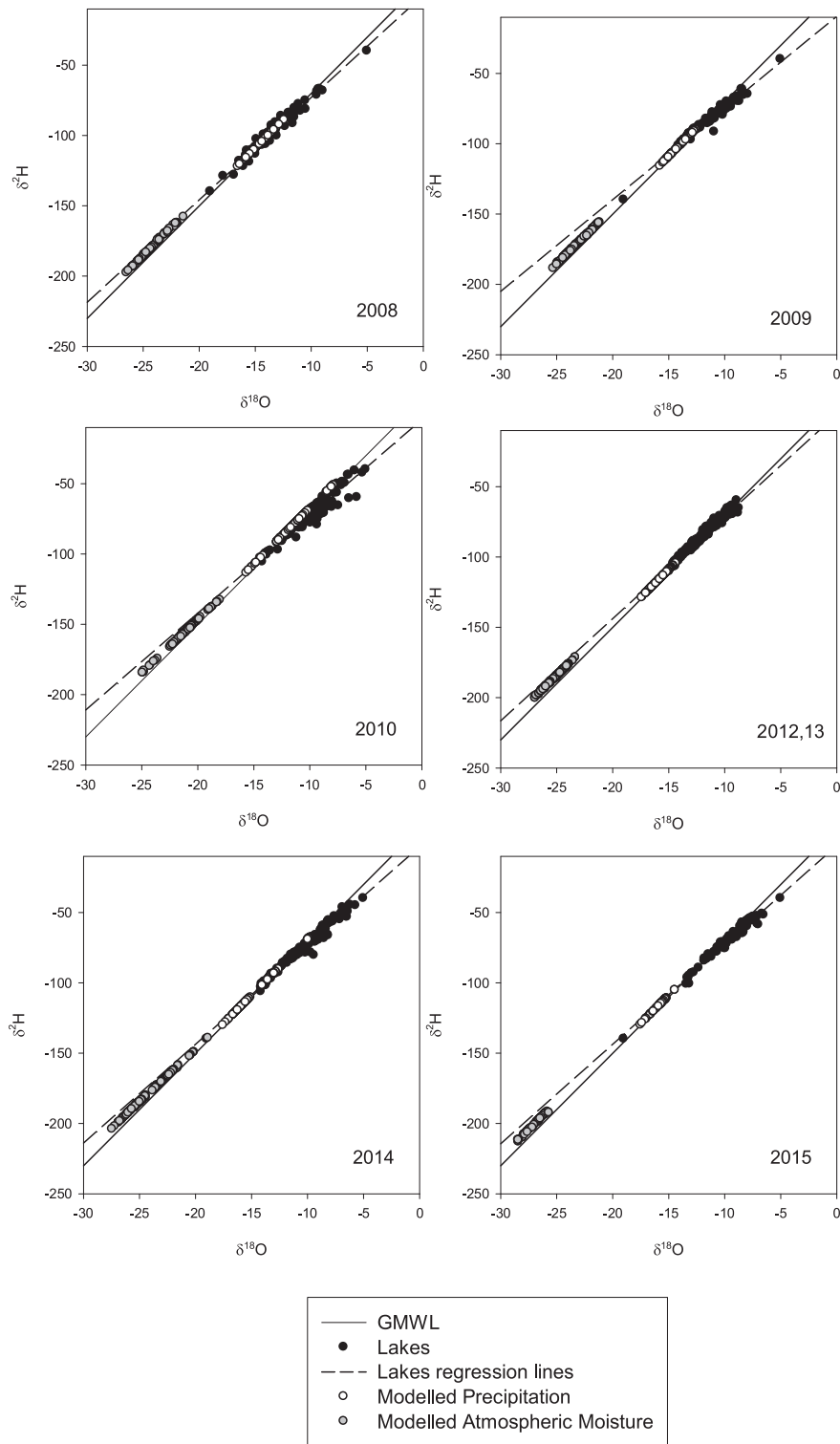


Fig. 6. Cross-plots of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ showing measured isotopic composition of lake water, modelled precipitation and evaporation-flux-weighted atmospheric moisture.

Table 1
Local evaporation lines for the study area, by year.

Year	LEL	r ²	n
2008	$\delta^2H = 7.28\delta^{18}O - 0.14$	0.964	77
2009	$\delta^2H = 6.52\delta^{18}O - 9.40$	0.976	114
2010	$\delta^2H = 6.88\delta^{18}O - 4.38$	0.937	128
2012,13	$\delta^2H = 7.25\delta^{18}O + 1.36$	0.975	205
2014	$\delta^2H = 7.02\delta^{18}O - 3.15$	0.977	147
2015	$\delta^2H = 7.07\delta^{18}O - 2.30$	0.976	78
All data	$\delta^2H = 6.98\delta^{18}O - 3.17$	0.969	749

humidity in coastal areas. Overall offset from the GMWL along LELs is also subdued compared to observations made in the aforementioned continental surveys, reflecting lower evaporation losses as discussed below.

3.4. Regional water balance outputs and gradients

Evaporation/inflow is shown to range from 0 to more than 80%, although the majority of lakes fall in the range of 0–20%, and the

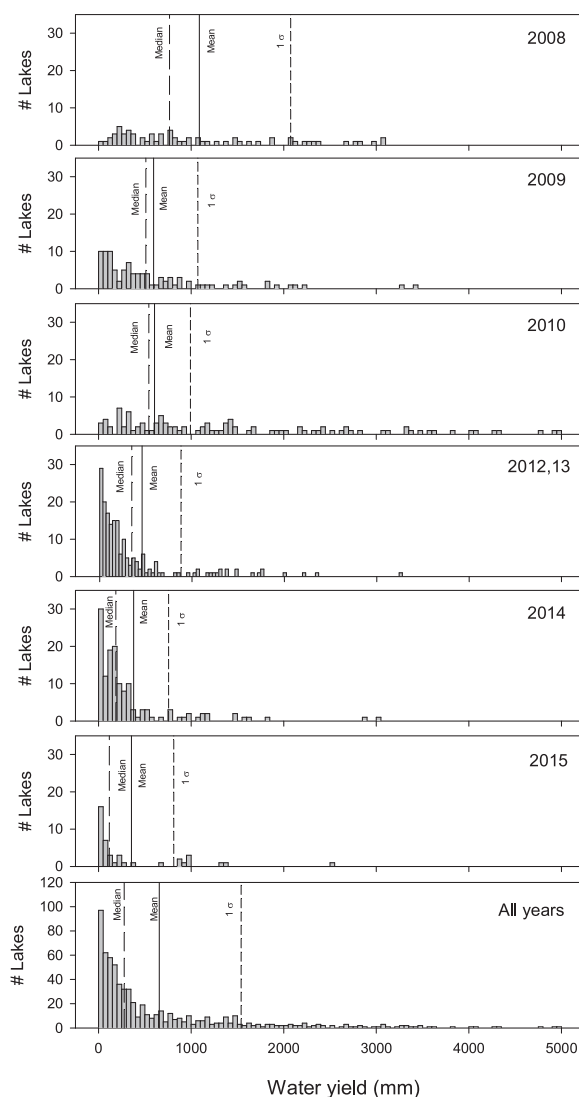


Fig. 7. Histograms showing distribution of calculated water yield for lakes overall and by year of sampling, 2008–2015.

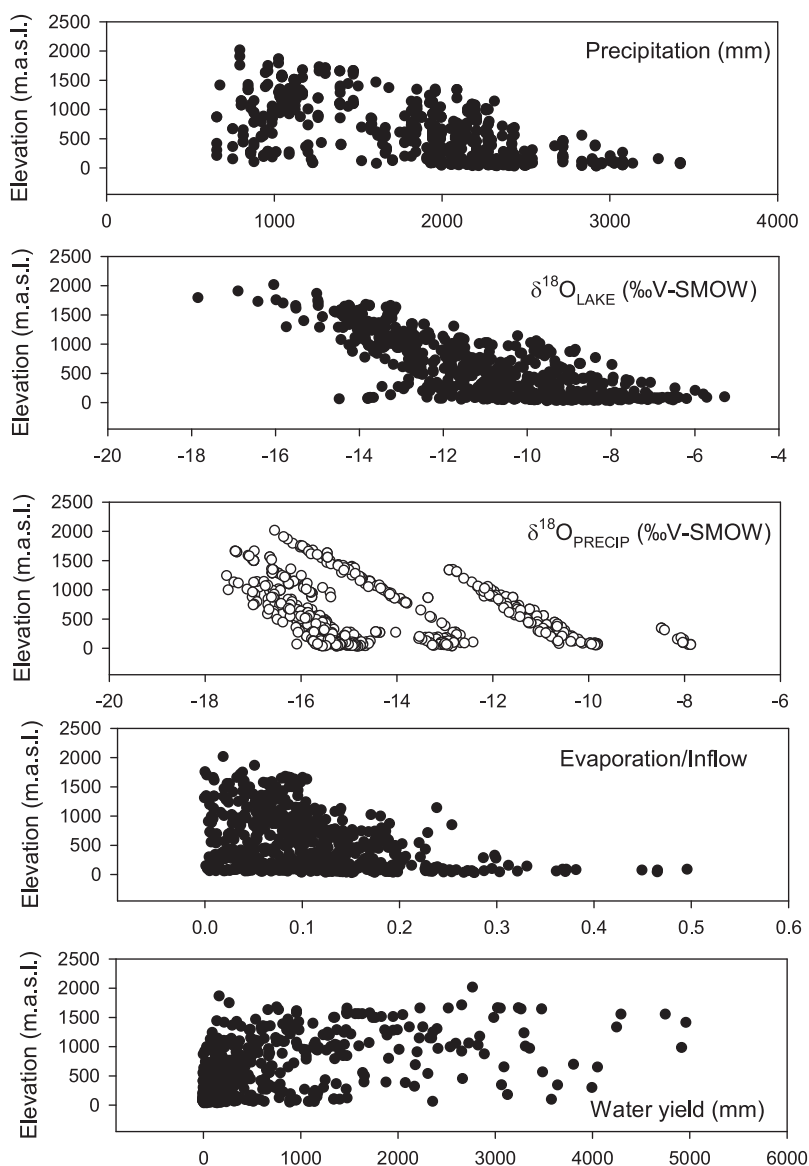


Fig. 8. Plots showing the elevation-related patterns in precipitation, $\delta^{18}\text{O}$ in lakes, $\delta^{18}\text{O}$ modelled in precipitation, calculated evaporation/inflow and calculated water yield. Similar trends are noted for $\delta^2\text{H}$ (not shown).

median is close to 9.6%. Evaporation/inflow is a sensitive indicator of the partitioning of water between liquid and vapour outflow, and as such reveals that lake evaporation is much less important for most watersheds in coastal B.C. than liquid discharge, the latter being predominantly as surface outflow *via* channelized streams, given the shallow soil development and dominance of bedrock in most areas. Distribution of evaporation/inflow is found to be slightly positively skewed (Fig. 4e), as noted in previous surveys in northwestern Ontario and Alberta (Gibson et al., 2015b, 2017).

Water yields for each yearly survey and for the entire dataset reveal positively skewed distributions in all cases (Fig. 7). Similar skewness has been observed in previous surveys in continental Canada (Gibson et al., 2010a, 2010b, 2015b, 2017). Overall, water yield was found to range from near zero to 5000 mm yr^{-1} , averaging 656 mm with a standard deviation of 884 mm . The median was 277 mm .

While there are a few lakes with high water yield, the results indicate existence of a large population of lakes that have significantly lower water-yield than average. Several of the lakes at higher elevation also appear to have water yield values that exceed mean annual precipitation, which may reflect uncertainty in basin areas or other model parameters, anomalous precipitation received in some areas during the study year (or prior years), and/or augmentation of runoff by glaciers, perennial snowpack, or glaciogenic groundwaters. The augmentation of runoff sources does not likely explain the higher water yield values predicted in parts of Vancouver Island with a warmer climate and lower elevation mountains. Here, uncertainty in model parameters such as isotopic composition of precipitation may be more important. Excessively-high water yields in these areas may also indicate heightened

sensitivity of the model at high relative humidity, which is expected based on previous assessments of the model (e.g. Gibson et al., 2002). However, Bemrose et al. (2009) also show that water yield based on river gauging may exceed observed precipitation by up to 25% for coastal areas of northern B.C. so this may be a more general sign of uncertainty in precipitation amounts as well.

Elevation, which is also significantly correlated with distance from the coast, is found to be a dominant driver of precipitation, lake and precipitation isotopic compositions, evaporation/inflow and water yield across the study region (Fig. 8). For precipitation, values for sites between sea level and 500 m are found to span the full range observed across the region (700–3500 mm), whereas the upper limit of precipitation amount becomes truncated at 2500 mm at mid-range elevations (500 and 1500 m), and is in all cases less than 1500 mm at higher elevations (above 1500m). This is an expression of the classic rainout process for the coastal mountain ranges.

Isotopic composition of precipitation (Fig. 8c) is shown to be strongly correlated with elevation, which is evidence of the isotope-altitude effect (Dangaard, 1964; Gat 1996). In this study, precipitation was modelled for each sub-region (each year) based on the method of Bowen and Wilkinson (2002) fitted to regional precipitation data from CNIP (Birks and Gibson 2009). This method has been shown to reproduce globally observed gradients in latitude and elevation. Overall the interpolated model data capture the effect of air masses being transported from the Pacific Ocean over the coastal B.C. ranges, and the associated removal of moisture from the atmosphere as a result of cooling of air masses and related isotopic fractionation.

Values and ranges in isotopic composition of lake water were also found to be elevation dependent. In general, high elevation lakes were found to be more depleted in $\delta^{18}\text{O}$ (Fig. 8b) and $\delta^2\text{H}$ (not shown). Higher elevation lakes were typically less evaporated, had more depleted input waters including precipitation and precipitation-derived surface and groundwater inputs from their catchments, and therefore were less isotopically enriched. Lower elevation lakes had more isotopically depleted precipitation sources and showed a larger range in isotopic composition as water balance factors were evidently more important spatially in determining the isotopic composition of the lakes. A unique group of low elevation lakes with depleted $\delta^{18}\text{O}$ (Fig. 8b) are large, fjord-type lakes suspected of being fed by springs originating at higher elevations.

Evaporation/inflow variations with elevation largely mimic the patterns exhibited by isotopic composition of lakes (Fig. 8d). Evaporation/inflow shows a narrow range for high elevation lakes and a larger range for low elevation lakes, most probably owing to the greater influence of lake and watershed configuration on surface water storage and evaporation in flatter, non-alpine areas. Such patterns have not previously been described for the region.

While detailed annual water yield estimates have been reported and mapped for the study region from river discharge data (Bemrose et al., 2009), no previous studies have specifically focused on characterizing water yield to lakes. We note that water yield based on 1971–2000 river discharge measurements ranges between ~ 1000 to 4300 mm yr^{-1} for our study region, and evidently increases towards low-elevation, hyper-maritime coastal areas where rainfall is highest. In contrast, our dataset clearly shows a significant positive correlation between elevation and water yield to lakes (log transformed), with an r value close to 0.518 ($p < 0.001$). We postulate that this may be due to greater potential for disconnection between lakes and rivers in low lying areas with lower slope, and better connectivity between lakes and rivers in steeper, higher elevation areas. Rivers are commonly observed to originate from lakes, often proglacial lakes at higher elevations. While beyond the scope of this article, a systematic analysis of specific watershed configurations would be of value for verifying this preliminary assessment.

We also note from our dataset that evaporation-flux-weighted temperature is negatively correlated with elevation, but does not appear to be a dominant driver of the derived water balance parameters.

3.5. Drivers of water balance and water quality

We further investigated the relationships between physical and geochemical properties, land cover, isotopic characteristics and derived water properties to investigate and better understand controlling processes in the lakes and their watersheds. A Spearman rank order test was used to test correlations as several of the variables were non-linearly related or were not normally distributed. A colour-coded matrix illustrates the strength and direction of correlation between significantly related variables (Fig. 9). Note that numerous relationships (276) are tested in this exercise, with significance assessed using an adjusted p value of 0.00005 with the Bonferroni correction applied.

Summarizing the apparent physical drivers of water balance, we note that EI.18O (E/I) is positively correlated with P and RH.FW, as well as Old.Forest but negatively correlated with Ele and Sub.Alpine. Alpine and Sub.Apline were highly correlated and so show similar patterns. Water yield (WYlog10) is positively correlated with Ele, E.m, LAWAR, and F.Water and negatively correlated with P, RH.FW, Old.Forest, and WA. For the multi-year survey, raw isotopic data (d18OL) are positively correlated with evaporation/inflow and negatively correlated with water yield. Overall, it appears that as distance from the coast and elevation increase, lakes tend to receive proportionately greater runoff from their watersheds, and the amount and variability of water loss by evaporation (E/I) is reduced. In contrast, coastal areas with lower elevations tend to have a wider range in E/I and increased evaporation losses. Based on the correlation analysis it appears that vegetation is only a minor water balance differentiator across this biogeoclimatic region. A weaker relationship evident in the dataset is for increase in F.Water and LA and reduced WA with increased proportions of Alpine and Sub.Alpine land covers, thereby producing an increase in LAWAR, although it is not clear at the present time whether this bias is reflective of shifts in lake population across the region, or how this may affect the regional water balance trends.

Several interesting observations also emerge from examining correlation of the chemical characteristics of the lakes. First of all, it is important to note that PSS for lake water, an indicator of sea spray aerosol influence (see Wadleigh et al., 1994), is found to be positively correlated with P, RH.FW, and negatively correlated with Ele, suggesting as expected that chemistry of the lakes is driven by continentality and distance from the ocean. This pattern is also retained in many of the chemical properties including EC, Cl, Na

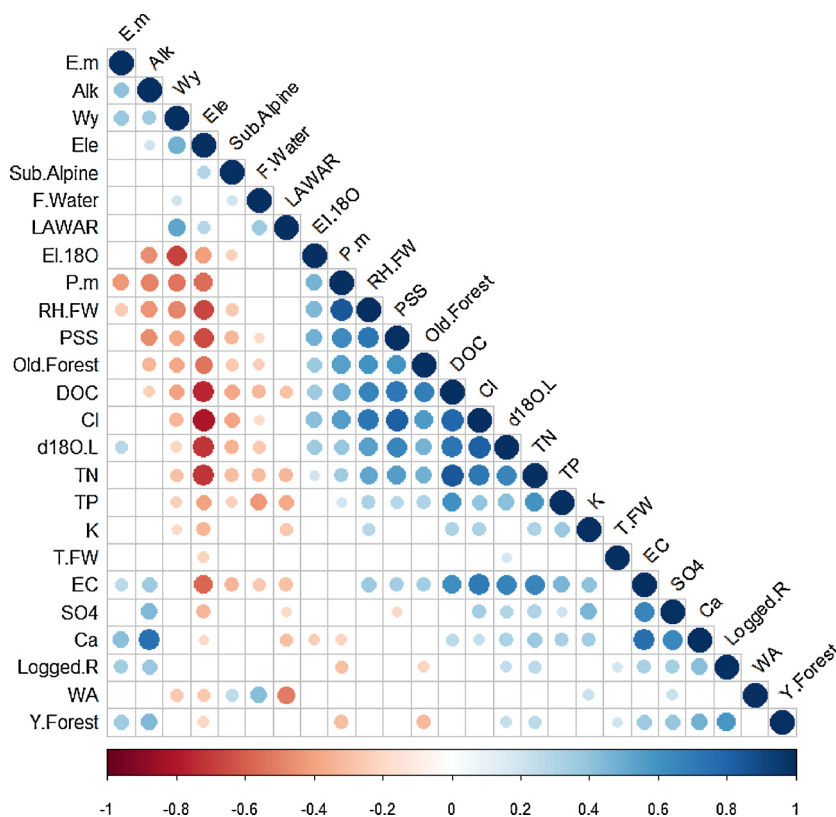


Fig. 9. Spearman correlation matrix for physical, geochemical, isotopic variables and land cover. Only significant correlations are shown with coloured circles. Colour, intensity and size of symbol are proportional to correlation coefficients, with negative correlations shown in red and positive in blue. See text for definition of parameters. Note that WY and WA, which are highly skewed are transformed to Log₁₀ scale. The transformation significantly improves the correlation of WY. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(not shown but comparable to Cl), and to some extent TN, TP, and DOC. Elevated nutrients and DOC in the lower elevation lakes are attributed to lush vegetation in the coastal Western Hemlock zone, occurrence of significant wetlands and organic soils as compared to the Mountain Hemlock zone, and longer periods of in-lake productivity.

PSS is negatively correlated with F.Water, Ele, and WY. Chemical properties that appear to be unrelated to PSS include Ca, Mg (not shown but similar to Ca), SO₄, and K, suggesting that these may be controlled by weathering processes and water-rock interaction. Alkalinity (Alk) is negatively correlated with PSS and is commonly higher in carbonate-rich terrains. pH (not shown) was found to be positively correlated with Alk and is weakly correlated with Ele and continentality. Both total base cations and the non-marine base cation fraction are found to decrease inland and with Ele, Alpine and Sub.Alpine, which suggests enhanced buffering potential in coastal areas as compared to high elevation areas inland. Nutrients and DOC concentration in the lower elevation lakes are also elevated compared to the higher elevation lakes. While not confirmed, this may be the result of greater vegetation cover across the watershed and longer periods of in-lake productivity.

The PCA results indicate that the first two axes, Dim1 and Dim2, account for 43.6% of variation within the entire dataset (Fig. 10). The horizontal axis (Dim1) differentiates lakes mainly according to Ele, pristine land cover classes (Sub.Alpine, F.Water, Old.Forest), moisture indicators (P, RH.FW) and marine influenced chemistry (PSS, Cl, DOC). In contrast, the vertical axis (Dim2) captures variability in E, disturbed land classes (Logged.R, Y.Forest), as well as the remaining ionic chemistry, including EC, Ca, SO₄, and Alk. As such, Dim2 captures variations in carbonate and sulfate species. TN and TP are influenced by both dominant axes as are the water balance indicators (EI.18O, WY, d18OL). One of the interesting results of the PCA analysis is that Vancouver Island lakes sampled in 2010 are visibly offset from the rest of lakes, plotting predominantly in the upper quadrants (Fig. 10). Carbonate and sulfate species are more prevalent in these lakes, which is attributed to predominance of sedimentary (43%) and volcanic rocks (50%) in these systems, as compared to silicate dominated mainland sites in the Pacific ranges (sampled in 2009) and Kitimat ranges (sampled 2012–2015) where intrusive igneous and metamorphic rocks are more common. Samples from the mainland areas of the Georgia Basin (sampled in 2008) are distinguished by stronger elevation control as sampling sites there ascend the Cascade Range.

Generally, higher elevation lakes contained the lowest concentrations of base cations and major anions, the concentrations of which are driven largely by marine sources, but is also likely reinforced by decreases in chemical weathering rates for high altitude lakes (Drever and Zobrist, 1992; Kamenik et al., 2001). While critical loads of acidity are expected to be dependent on both WY and

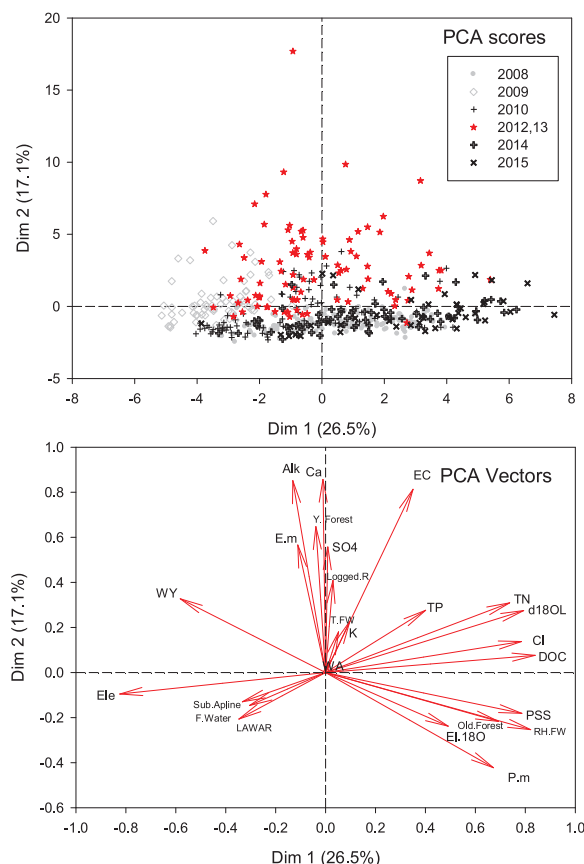


Fig. 10. (a) PCA score plot for lakes, and (b) vector loadings for variables used in the analysis. Lakes are differentiated by year of sampling. Note that 2010, highlighted in red, corresponds to Vancouver Island. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

non-marine base cations (see [Henriksen et al., 2002](#)), increased runoff with continentality is expected to only partially compensate for gradients in base cations, and as such we expect critical loads to be higher in coastal areas and reduced inland. In particular, the marine influence, lithology and chemical weathering appear to be the most influential water quality source determinants. It should also be noted that more vigorous watershed runoff to lakes at higher elevations increases throughflow, reduces contact time for weathering and contributes to relative dilution of lake waters, which is also expected to make high elevation, inland watersheds sensitive to acidification.

Based on a preliminary evaluation we attribute the dissimilar water yield patterns to be the result of low elevation lakes being relatively disconnected from the regional river networks, and hence having lower water yield values than high elevation lakes. High elevation lakes tend to be located in glacially scoured valleys, serve as focal points capturing runoff from upstream areas, and constitute much of the source water for many alpine and sub-alpine streams...In addition, the water yield estimates based on river gauging network may not be representative of smaller watersheds, particularly high-elevation sub-basins examined in this study.

4. Summary and conclusions

Geochemistry and isotopic composition was measured in 783 water samples collected by helicopter from 560 lakes in coastal B.C. and Vancouver Island during 2008–2015. Lakes and watershed areas were delineated and physical and land cover characteristics of the watersheds were compiled in a database. Repeat sampling in a subset of 100 lakes was used to confirm that isotopic characterization was meaningful based on one-time sampling for most lakes. An isotope mass balance method was applied to estimate the evaporation/inflow and water yield to lakes and provides a novel perspective on the regional hydrology of lake and watershed characteristics across the coastal mountains of B.C. and Vancouver Island. Notably, elevation is found to be a dominant driver of water yield, although the observed patterns appear to contrast with river gauge measurements which suggest highest runoff occurs in coastal areas. Our results imply that low-elevation lakes, as compared to high-elevation lakes, must be significantly more disconnected from the regional river drainage networks due to lower slope and more disorganized drainage. Geochemical drivers across the region include sea spray, lithology, weathering, and elevation, the latter being influential on lake flushing. Distinct geochemical properties are noted for Vancouver Island lakes as watersheds in this area are typically dominated by sedimentary and volcanic rocks,

whereas mainland lakes in the coastal mountain ranges are dominated by intrusive and metamorphic rocks.

Overall, this study has contributed to new understanding of hydrological processes in coastal areas of British Columbia, and has identified regional trends in water balance of lakes, as well as physical and chemical properties that may influence critical loads of acidity. This study has extended application of an isotope mass balance method that has been widely used in continental regions of Canada to coastal areas, describing similar but subtly different isotopic enrichment effects.

The major limitation of the analysis is the lack of a spatially-distributed precipitation isotope network in the region. If established, such a network would potentially allow isotope balance methods to be applied with reduced uncertainty, and would also serve to better isolate isotopic variations related to rainout versus the subsequent effects of open-water evaporation. To further improve the understanding of spatial variations in acid sensitivity, a steady-state critical loads assessment is being developed to systematically integrate and map the base cation buffering information and water yield estimates across the region. Additional analysis will also target comparison of water yield derived from the river gauging network and this lake network to better understand differences in the runoff characteristics of the region.

As described, the method is a transferable approach for assessing water balance and water quality-water quantity relationships at the regional scale in remote or poorly-monitored, lake-rich regions.

Conflict of interest

None.

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